# A NOTE ON THE ENERGY DIFFERENCE OF TRANS AND GAUCHE CONFIGURATIONS IN 1, 2-DICHLOROETHANE AND 1, 2-DIBROMOETHANE IN THE LIQUID STATE

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**ABSTRACT.** The temperature dependence of the intensity ratios of the Raman lines 755 and 654 $cm^{-1}$ in liquid 1, 2-dichloroethane and the lines 665 and 551 $cm^{-1}$ in liquid 1, 2-dibromoethane due respectively to trans and gauche molecular configurations in each of the compounds has been studied with a self recording photoelectric spectrometer and the results obtained are in fair agreement with those reported by other workers. From an analysis of the results it is pointed out that the conclusion drawn by previous workers that there is no energy difference between the two configurations in ethylene dichloride (1, 2-dichloroethane) in the liquid state, is not justified and the simple explanation for the lowering of the energy of the polar gauche form due to excess of electrostatic energy in the liquid state is not valid. An expression for the temperature dependence of the intensity ratio of the pair of Raman lines in each of the two compounds in the liquid state has been obtained after taking due consideration of the effects due to intermolecular potential energy and the energy difference between the two configurations in the free molecule on the equilibrium population of the trans and gauche molecules. The effective energy difference between the two configurations has been obtained for both the compounds and is found to be 446 cal/mole for 1, 2-dichloroethane and 1065 cal/mole for 1, 2-dibromoethane in the liquid state.

## INTRODUCTION

The energy difference and the population ratio of trans and gauche molecular configurations in 1, 2-dichloroethane and 1, 2-dibromoethane in the gaseous, liquid and solid states have been studied by the methods of Raman spectroscopy, Infrared absorption and dielectric measurements and a review of the works done on the rotational isomerism in the substituted ethanes is given by Sheppard (1959). It is well known that in the cases of 1, 2-dichlore- and 1, 2-dibromoethanes in the vapour phase the energy of the gauche configuration is higher than that of the trans-configuration and in the liquid state the energy of the gauche form decreases appreciably such that in liquid 1, 2-dichloroethane the energy difference between the two configurations is almost zero. Following Watanabe *et al*'s (1943) suggestion that the excess electrostatic energy of the polar gauche con-

figuration is responsible for the lowering of the energy of the gauche configuration in the liquid state, Wada (1954) calculated the lowering of energy of the gauche configuration of 1, 2-dichloro and 1, 2-dibromoethanes in the liquid state and obtained rough quantitive agreement with the experimental results. However, Mazumder (1953, 1959) pointed out that the population ratio of the two configurations in the liquid is not determined solely by the energy difference between them and the effect of the intermolecular field on the rotatinal isomers should also be considered in determining the ratio.

In order to find out the influence of the intermolecular field it was necessary to obtain reliable values of the intensity ratios of the Raman lines due to trans- and gauche molecules at several temperature intervals. As this had not been reported by previous workers, the Raman spectra of 1, 2-dichloroethane (ethylenedichloride) and 1, 2-dibromoethane (ethylene dibromide) in the liquid state at several temperatures have been reinvestigated with a self recording photoelectric spectrometer and the results obtained together with a discussion of the results are presented in this paper.

## EXPERIMENTAL

Pure samples of ethylene dichloride and ethylene dibromide obtained respectively from B.D.H. (U.K.) and Merck (W.G.) were throughly dried with fused calcium chloride and then fractionated. The proper fractions were distilled under reduced pressure immediately before use for reducing background interferences due to the presence of dust particles, water vapour and other trace impurities. The liquids were sealed in long double jacketted glass tubes with plain windows and their temperatures were controlled within 1°C by circulating water from a thermostat. The spectrum due to the scattered radiations was recorded with a self-recording grating monochromator designed by Sirkar *et al* (1961). However, the d.c. amplifier used by them was replaced by an A. C. amplifying device and the negative D.C. voltage to the E.M.I. photomultiplier tube was obtained from a bank of dry batteries instead of the electronic power supply. The width of the entrance slit of the monochromtor was about 15 $cm^{-1}$ in the 4500 Å region while the exit slit was 30 $cm^{-1}$ wide. The spectra were scanned at the rte of about 3 $cm^{-1}$/sec.

The Raman spectra of the two compounds at different temperatures were recorded several times in order to reduce the error in the measurement of the intensities of the Raman lines as far as possible. The intensity ratio of the pair of of Raman lines was determined from the peak values in each case.

## RESULTS

The ratio of the intensities ($I_{\Delta\nu t}/I_{\Delta\nu g}$) at different temperatures of the Raman lines 755 and 654 $cm^{-1}$ respectively due to the trans and gauche molecular con-

figurations of ethylene dichloride in the liquid state are given in table 1 while table 2 contains the intensity ratios of the Raman lines 665 and 551 $cm^{-1}$ due to the same two configurations in liquid ethylene dibromide at various temperatures. One representative record of the pair of Raman lines due to trans and gauche molecular configurations for each of the two compounds is shown in figures 1(a) and (b).

Table 1

1, 2-dichloroethane (liquid)

| T°K | $\frac{I_{755}}{I_{655}}$ | Energy difference (Cal/mole) | | Reference |
|---|---|---|---|---|
| | | without intermolecular interaction | with intermolecular interaction | |
| 286<br>303<br>333<br>363 | 1.21<br>1.24<br>1.265<br>1.30 | −180 | 446 | Present authors |
| 303<br>400 | 1.80<br>2.00 | −250 | | Mazumder (1953) |
| 278<br>369 | 1.23<br>1.28 | −100 | | Rank *et al.* (1949) |
| 258 | 1.50 | — | | Watanabe *et al.* (1942) |
| 298<br>323 | 1.80<br>2.10 | −230 | | Morino *et al.* (1941) |

Table 2

1, 2-dibromoethane (liquid)

| T°K | $\frac{I_{665}}{I_{551}}$ | Energy difference (Cal/mole) | | Reference |
|---|---|---|---|---|
| | | without intermolecular interaction | with intermolecular interaction | |
| 303 | 7.0 | | | Mazumder (1959) |
| 288<br>371 | 7.81<br>6.00 | 740±80 | | Rank *et al.* (1949) |
| 283<br>286<br>308<br>340<br>359 | 9.17<br>8.90<br>8.02<br>7.21<br>6.62 | 840 | 1065 | Present authors |

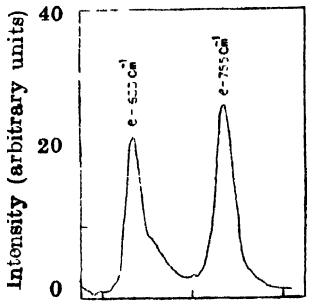



Figure (1a)

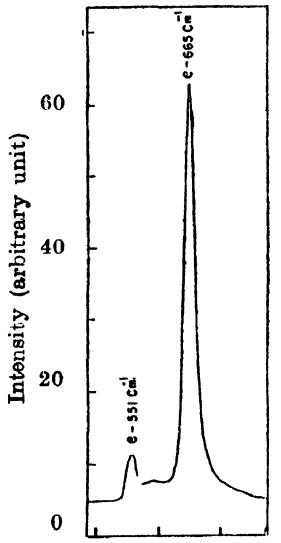



Figure (1b)

In each of the Tables the values of the ratio reported by other workers are given for comparison. The plots of log $(I_{\Delta\nu t}/I_{\Delta\nu g})$ vs $1/T$ for the two compounds are depicted in figure 2 and the values of the slopes of these curves generally identified with the energy difference between the two configurations, together with those obtained by other workers are also shown in the respective tables.

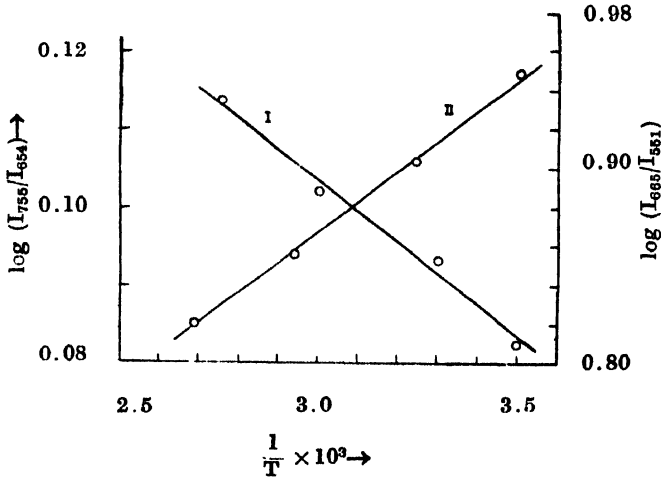



Figure 2.

## DISCUSSION

It is seen from tables 1 and 2 that in the case of ethylene dibromide in the liquid state, the value of the intensity ratio of the Raman lines 665 and 551 $cm^{-1}$ i.e. $I_{665}/I_{551}$ increases fairly rapidly with decrease in the temperature of the liquid and in the case of liquid ethylene dichloride the ratio $I_{755}/I_{654}$ decreases slowly as the temperature is lowered. The results for the lowest and the highest temperatures mentioned in table 1 fairly agree with those reported by previous workers. The value of the energy difference is positive for ethylene dibromide and negative for ethylene dichloride. Previous workers (Sheppard, 1959) concluded from their results that the energy difference between the gauche and trans configurations in ethylene dichloride in the liquid state is zero. The very fact, however, that the intensity ratio of the pair of Raman lines in liquid ethylene dichloride varies with temperature indicates that the energy difference is not zero. Hence the explanation (Wada, 1954) that the excess electrostatic self-energy of the polar gauche form is mainly responsible for the vanishing of the energy difference in the liquid phase is not tenable.

In order to examine the suggestion made by Mazumder (1953, 1959) it would be necessary to obtain an expression for the temperature dependence of the intensity of Raman lines due to trans and gauche configuration of the molecules in the liquid state, by taking into account the energy difference between the two configurations in the free molecule and the effect of various intermolecular interactions in the liquid. This is done in the following paragraphs.

It is well known that the intensity ratio of two Raman lines due respectively to trans and gauche configurations is given by $I_{\Delta\nu t}/I_{\Delta\nu g} = \lambda N_t^0/N_g^0$ where $\lambda$ is a constant and $N_t^0$, $N_g^0$ are respectively the populations of the vibrationless states in the two configurations. In the gaseous state $\frac{N_t^0}{N_g^0} \quad \frac{K_{gt}^0}{K_{tg}^0} = e^{\frac{\Delta E_g}{RT}}$ where $K_{gt}^0$, $K_{tg}^0$ are respectively the transition rates from the gauche to trans and trans to gauche configurations and $\Delta E_g$ (cal/mole) is the energy difference between the two configurations. In the liquid state the interactions between the polar gauche molecules changes the transition rate from $K_{gt}^0$ to $K_{gt}$ and the equilibrium ratio is given by $\left(\frac{N_t^0}{N_g^0}\right)_{liq} = \frac{K_{gt}}{K_{tg}^0}$

In the liquid state the interactions between the gauche molecules makes this configuration energetically more stable and all molecules would revert to this form but for the high potential barrier separating the two configurations in the free molecules. The interactions in the liquid state provides a well of depth $\Delta E_f$ cal/mole for the gauche moecules which affects the transition rate from the gauche to trans configurations. At any temperature ($T$) because of fluctuations

in the energy of the molecules some of the gauche molecules overcome the influence of the intermolecular interactions and change into the trans configuration. The rate at which the first process occurs, according to the theory of reaction rates is given by $K_1 = ATe^{-\frac{\Delta E_f}{RT}}$ where $A$ is a constant and the rate of the second process is $K_{gt}^0$ whence

$$K_{gt} = K_1 K_{gt}^0 = ATe^{-\frac{\Delta E_f}{RT}} . K_{gt}^0 \quad \text{and}$$

$$(N_t^0/N_g^0)\text{liq} = K_{gt}/K_{tg}^0 = ATe^{-\frac{\Delta E_f}{RT}} . K_{gt}^0/K_{tg}^0$$

substituting

$$\frac{K_{gt}^0}{K_{tg}^0} = e^{\frac{\Delta E_g}{RT}}$$

we get,

$$\left(\frac{N_t^0}{N_g^0}\right)\text{liq} = ATe^{\frac{\Delta E_g - \Delta E_f}{RT}} = ATe^{\frac{\Delta E_l}{RT}}$$

where $\Delta E_g - \Delta E_f = \Delta E_l$ (cal/mole) may be called the effective energy difference in the liquid state.

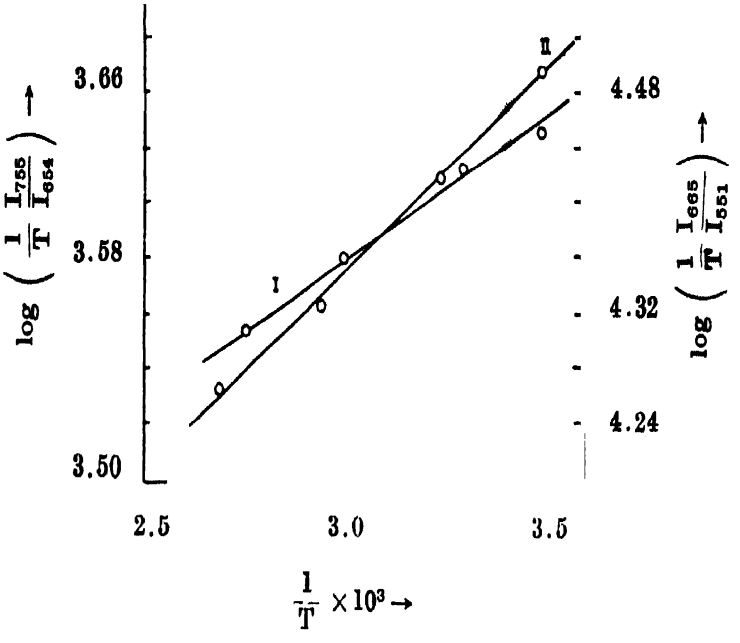
Since $I_{\Delta\nu t}/I_{\Delta\nu g} = \lambda \frac{N_t^0}{N_g^0}$ for the gaseous or the liquid states we have

$$\frac{I_{\Delta\nu t}}{I_{\Delta\nu g}} = \lambda ATe^{\frac{\Delta E_l}{RT}}$$

and the plot of $\log\left(\frac{I}{T}\frac{I_{\Delta\nu t}}{I_{\Delta\nu g}}\right)$ vs $1/T$ should yield a straight line the slope of which gives the value of $\Delta E_l$.

Such plots in the case of ethylene dichloride and ethylene dibromide are shown in figure 3. The values of $\Delta E_l$ obtained from these graphs are 446 cal/mole for ethylene dichloride and 1065 cal/mole for ethylene dibromide. Thus it is found that according to the discussions given above the gauche configurations even in the case of liquid ethylene dichloride has the higher energy which is in contrast to the conclusions mentioned before.

The potential energy due to the intermolecular and other interactions are obtained from the relation $\Delta E_f = \Delta E_g - \Delta E_l$. Using the generally accepted values of $\Delta E_g = 1270$ cal/mole and 1700 cal/mole respectively for ethylene dichloride and ethylene dibromide in the gaseous state, the values of $\Delta E_l$ is found to




be 820 cal/mole for ethylene dichloride and 635 cal/mole for ethylene dibromide. These values are of the same order and though not large do not seem unreasonable.

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